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Overview of Smoke Toxicity Testing and Regulations

JESSE J. BEITEL
CRAIG L. BEYLER
LAWRENCE A. MCKENNA

Hughes Associates, Inc.
Baltimore, MD

FREDERICK W. WILLIAMS

Naval Technology Center for Safety and Survivability Branch
Chemistry Division

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Jesse J. Beitel,* Craig L. Beyler,* Lawrence A. McKenna,* and Frederick W. Williams

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Historically, more people are injured and die from fire combustion products than from direct heat/flame exposure. Evaluations have shown that personnel remote from the source of a fire are particularly at risk from fire effluent from post-flashover fire scenarios.

Various test methods have been developed to assess the toxic potential of smoke from buring materials. These test methods are sensitive to the fire exposure (e.g., smoldering vs. flaming), size of the sample, and translation of the measured gases to toxic potential to humans in a real-scale scenario. Test methods use either bioassay methodologies (animal testing) or analytical techniques to establish toxic potency of buring materials. Available test methods are reviewed. Few jurisdictions currently regulate material toxicity in terms of specific criteria.

Options for evaluating material toxic potency are outlined. These options should be considered in terms of the material use and hazard, other methods to reduce toxic hazard (e.g., by carefully regulating material ignition, flame spread, and heat release), and the introduction of new/novel materials for shipboard applications.

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CONTENTS

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OVERVIEW OF SMOKE TOXICITY TESTING AND REGULATIONS

1.0 INTRODUCTION

The issue of the toxicity of the smoke resulting from the combustion of materials is not new. It has been recognized that the greatest number of fire deaths are due to the toxic effects of smoke and not to the thermal effects of the fire.

> "Every year in the United States about 10,000 people lose their lives because of fires. It has been observed and commented upon that many of these victims are not burned but succumb to the effects of 'smoke' and gases. When deaths from this source are reported, it is notable that almost never has it been found, specifically, what poisonous gas or gases caused the fatality"[1].

This statement was made almost sixty-three years ago and published in the Quarterly of the National Fire Protection Association. It serves to remind us that the issue has been recognized for many years and that, despite great effort, the complexity surrounding the issue of smoke toxicity is such that it has not yet been fully resolved.

Currently, there is very little regulation based on the smoke toxicity of materials or products. This is true for both the U.S. Navy and the civilian sector; however, the question of "should regulation be imposed?" is continually asked by regulators.

2.0 OBJECTIVE

The objective of this paper is to provide an analysis of the smoke toxicity issue such that a direction for US Navy regulations can be determined with respect to smoke toxicity. This analysis includes a review of existing regulations, test methods, and the potential use of tests for regulatory purposes.

Since the majority of the work in this area has been performed in the civilian sector, this will form the basis of this review, but the work is applicable to the US Navy and will be placed in context with the US Navy's unique problems.

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3.0 BACKGROUND

3.1 Fire Death Statistics

Smoke inhalation and the toxicity of that smoke is the principal cause of fire deaths in the US. The classic study with respect to causes of fire deaths was by Berl and Halpin and involved an analysis of fire deaths in Maryland during the time period of 1972-1977 [2]. From the results, it was estimated that smoke inhalation, specifically carbon monoxide, accounted for approximately 75 percent of all fire deaths. While this study might have overstated the effects of carbon monoxide due to the measurement techniques, the basic results were accepted as valid.

Since 1979, the coding of US fire death certificates was revised to include a determination of burns versus smoke inhalation as a cause of death. Table 1 provides a summary of the reported causes of fire deaths for the period 1979 through 1992 [3].

Table 1. Burn vs. Smoke Inhalation Shares of Fire and Flame Deaths, 1979-1992

Year	Total	Smoke Inhalation		Burns		Other	
1979	5,998	3,515	(58.6%)	2,262	(37.7%)	221	(3.7%)
1980	5,822	3,515	(60.4%)	2,079	(35.7%)	228	(3.9%)
1981	5,697	3,501	(61.4%)	2,048	(35.9%)	148	(2.6%)
1982	5,210	3,396	(65.2%)	1,683	(32.3%)	130	(2.5%)
1983	5,039	3,245	(64.4%)	1,654	(32.8%)	140	(2.8%)
1984	5,022	3,277	(65.2%)	1,625	(32.4%)	121	(2.4%)
1985	4,952	3,311	(66.9%)	1,498	(30.3%)	143	(2.9%)
1986	4,835	3,328	(68.8%)	1,415	(29.3%)	92	(1.9%)
1987	4,710	3,307	(70.2%)	1,301	(27.6%)	102	(2.2%)
1988	4,965	3,480	(70.1%)	1,378	(27.8%)	106	(2.1%)
1989	4,723	3,308	(70.0%)	1,311	(27.8%)	103	(2.2%)
1990	4,181	2,986	(71.4%)	1,138	(27.2%)	57	(1.4%)
1991	4,126	2,977	(72.2%)	1,078	(26.1%)	70	(1.7%)
1992	3,966	2,866	(72.3%)	995	(25.1%)	105	(2.6%)
Percent Change 1979-1992	-34%	-18%		-56%		-52%	

The data show that approximately three-quarters of the 1992 fire deaths are due to smoke inhalation. Even though the total number of deaths are declining, deaths due to smoke inhalation is becoming a greater percentage. These data reinforce the position that the majority of fire deaths are caused by smoke inhalation and the victims are generally remote from the initial fire.

Additional analysis of fire death statistics [3] show that most fire victims (65.8%) killed by smoke inhalation are located remote from the room of fire origin and are killed by fires that attain flashover in the room of fire origin.

Table 2 provides an analysis of fire deaths aboard US Navy surface ships for the period of 1960 - 1986. These data were developed through a survey of JAG reports [4,5].

Table 2. Causes of Fire Deaths Aboard US Navy Surface Ships, 1960-1986

Number of Deaths	Cause of Deaths
85	"Asphyxiation," "smoke inhalation/asphyxiation," "CO poisoning," or CO/CO_2 or Smoke Asphyxiation"
35	"Other," "Burns," etc.
199	"Unspecified" cause
319	Total

These data show that for "specified" fire deaths, smoke inhalation comprises 70.8% of the deaths. Based on the JAG reports data, it is not possible to determine either the location of the fire victims with respect to the fire, or the size of the fire which caused death.

Based on both the civilian and US Navy fire death data, however, it is apparent that the smoke toxicity is the most important factor in fire deaths.

3.2 Smoke Toxicity Research

Prior to the late 1970's, the study of the toxicity of the products of combustion of "ordinary" fires evolved slowly. The early approaches basically consisted of analysis of various components of the smoke such as carbon monoxide, carbon dioxide, nitrogen, and sulfur oxides. At that time, however, very limited data about the effects of short-term human exposure to these chemicals were available, so assessments of fire toxicity were based on the Threshold Limit Values (TLV's) and other industrial workplace criteria [6].

Since the late 1970's, a great deal of attention has been drawn to this issue in the US. This attention was generated by several factors which included (1) a number of fires where large

numbers of people died from smoke exposure, and not from any exposure to the fire [7], and (2) the finding of unusual and severe symptoms beyond carbon monoxide poisoning in laboratory animals when exposed to the smoke from the combustion of an experimental product [8].

The initial regulatory response to the issue in the building code sector was requirements for materials to be "no more toxic than wood" [9]. Research on the toxic effects of smoke was begun in earnest throughout the US. After several years, the requirements for materials to be "no more toxic than wood" were removed from most regulations because of the complexity of measuring and implementing this criterion.

There are two principal theories concerning why smoke toxicity appears to be an increasing problem, and these have led to two rather different approaches to the evaluation of smoke toxicity: materials based and combustion product based approaches [10].

The materials based approach holds that modern synthetic materials contain new toxic products that were not present in previous materials, and that in some cases these products may be very potent, exerting novel toxic effects at very low doses (the so-called 'supertoxicants'). This approach evolved largely from the discovery that, under certain fire conditions, a flexible polyurethane foam containing a phosphorous-based fire retardant and polytetrafluoroethylene (PTFE) evolved products with a very high toxic potency [8,11,12,13]. This approach led to the development of materials based toxicity tests that rank the toxicity of a material in terms of the rodent LC_{50}. LC_{50} is the lethal concentration required to kill 50 percent of the exposed animals.

The combustion product based approach holds that the basic toxic by-products of fires are much the same as always (i.e., CO, CO_2, hydrocarbons, etc.), but that the growth rate and evolution of these common toxicants is much greater in modern materials than in older materials. Under this theory, the best way to control the toxic hazard is to control such factors as ignitability, flame spread, and the rate of smoke evolution. This approach assumes that a "supertoxicant" does not exist.

3.3 Definitions

It would be useful to provide several definitions of terms that will be used throughout this paper. These terms have been defined by ASTM [14]:

Smoke toxicity – the propensity of smoke to produce adverse biochemical or physiological effects;

Toxic Hazard – the potential for physiological harm from toxic products of combustion. Toxic hazard reflects both the quantity of toxic products and the quality of those products which is given by toxic potency. Toxic hazard is not the only hazard associated with fire. Toxic hazard is not an intrinsic characteristic of a material or product, but will depend upon the

fire scenario, the condition of use of the material or product, and possibly other factors; and

Toxic Potency – a quantitative expression relating concentration and exposure time to a particular degree of adverse physiological response (for example, death) on exposure of humans or animals. The toxic potency of the smoke from any material, product, or assembly is related to the composition of that smoke, which, in turn, is dependant upon the conditions under which the smoke is generated.

3.4 Technical Obstacles

Fire is a highly complex and dynamic event. Every fire is different as can be readily observed in the results of various medium-scale and full-scale laboratory fire behavior test methods. This makes generalization of the fire event a difficult task, fraught with the risk of underestimating significant risk factors.

The characteristics of the smoke that a material produces when it burns are very dependent upon the way that it is burning. The mode of combustion, i.e., smoldering vs. flaming, makes a major impact on the smoke as does the availability of oxygen in the combustion zone. This results in significant differences in the effluents produced by a material burning in the pre-flashover fire environment and the post-flashover environment. These differences have been well documented in the literature for many years [15].

Given these changing conditions and hazards presented by real-world fires, it is important to recognize that any standard test method uses some critical assumptions in its design, and that these assumptions will make major differences in the output of the tests. If the assumptions are not appropriate for a given fire hazard analysis, then the predicted exposure will be in error. The critical issues upon which the prediction of smoke toxicity rest include the following:

1. The mode of combustion (i.e., smoldering vs. flaming, free burning vs. oxygen starved),

2. The configuration of the specimen (i.e., composite vs. single material, horizontal vs. vertical),

3. The use of animals to model human response to fire effluents,

4. The use of chemical analysis of fire gases to model human response,

5. The synergistic, or combined, effects of various chemical species on humans during simultaneous exposure,

6. The time varying production of various chemical species during the varying combustion process,

7. The length of exposure of the individual to the toxicant,

8. The physiology, make up, and condition of the individual(s) exposed to the smoke,

9. The presence or absence of other exposures, such as heat and reduced visibility.

Every standard test method must, by its very nature, make assumptions that become inherent in its design. The validity of those assumptions to a particular fire hazard analysis have a direct impact on the applicability of the results of the tests. The researchers involved in developing smoke toxicity tests are well aware of these limitations. In fact, most of the controversy within the fire research community on the subject of smoke toxicity has been focused on these very issues.

As our understanding of fire growth and behavior grows, we are better able to make intelligent and appropriate decisions to resolve these difficult issues. Extensive analysis of the causes of fatalities in fires has shown that the greatest danger to life, for those who are not intimate with the fire, occurs during the post-flashover phase of a fire. During this phase, the fire is acting as a huge pump, developing large quantities of effluents, and driving them far beyond the room or compartment of origin. Also during the post-flashover phase, the fire has a limited supply of oxygen for combustion, resulting in incomplete combustion that adds a variety of chemical species to the effluent that are not produced when excess oxygen is available for the combustion process. At the present time, there is a developing consensus that radiant exposure of the specimen is the most appropriate combustion modality. The following review of current toxicity test methods will show that the more recently developed tests have adopted radiant furnaces as the combustion method.

There also appears to be a general consensus that the most important toxicant in ordinary fires are Carbon Monoxide (CO), Oxygen (O_2) deprivation, and Carbon Dioxide (CO_2) along with Hydrogen Cyanide (HCN), Hydrogen Chloride (HCl), and Hydrogen Bromide (HBr) for materials where nitrogen, chlorine, or bromine are present in the formulation. Current understanding of the synergistic effects of common fire effluent gases has led to the widespread adoption of the fractional equivalent dose (FED), or "N-Gas Model," calculation technique [16,17,18]. Expressed mathematically, the technique is shown as follows:

$$FED = \sum_{i=1}^{n} \int_{0}^{t} \frac{C_i}{(Ct)_i} dt \tag{1}$$

where C_i is the concentration of the toxic species "i", and $(Ct)_i$ is the specific exposure dose required to produce the toxicological effect being modeled (i.e., death). Where the FED=1, it is

expected that the mixture of gaseous toxicant would be lethal to 50 percent of the exposed animals.

There also appears to be a consensus that it is possible that other, more exotic, species may be produced under some conditions, and that the test methods must check for this potential. Since it is impractical to analyze every specimen for every possible chemical species that may be toxic, animal models have been widely used for this purpose. There is an ongoing controversy over the ethics of using animals for these tests that is currently affecting the international standards development community.

Opinions concerning the utility of the tests range from those who believe that the tests are useless in estimating the real-world toxicity in a fire, to those who believe that small scale tests can be predictive of real-world hazards and so should be used for regulatory purposes.

4.0 TEST METHODS

The existing test methods can be grouped into three broad categories based on the size of the sample and the method of exposure (small scale tests, medium scale tests, and full scale tests), and two general classes based on the method of determining the impact of the toxicant on humans (bioassay and analytical techniques). General observations about each of these categories follow [6].

4.1 Small-scale Laboratory Tests

Small-scale test methods generally use samples of 100 grams or less. These tests are attractive for a number of reasons, not the least of which is their relatively low cost. Sample size and the combustion mode and exposure temperature can be very precisely controlled, and laboratory analytical instruments are readily available to assist in the analysis.

The relationship between small-scale tests and large-scale tests is quite uncertain at this time. This relationship depends on many variables, most notably the type of fire exposure (i.e., flaming or smoldering combustion) and the nature of the material being tested (i.e., is it being tested in its end-use configuration). All of the test methods reviewed for this report are small-scale tests since these are the only test methods that have been accepted for general use to date.

Small-scale test methods generally include the following:

1. Either the temperature or the heat flux that the sample is exposed to is carefully controlled,

2. Only a single material is tested at a time although in some instances a composite is used to reflect the end-use conditions,

3. The products of combustion that are evolved in the combustion chamber are transferred into the exposure chamber with minimal contact with transfer lines,

4. In bioassay methods, the animals are exposed to the products of combustion, either by head-only exposure or whole body exposure, and both the combustion atmosphere and the blood of the exposed animals are analyzed,

5. In the analytical methods, the combustion and sampling are generally performed in the same chamber or box, and samples are drawn from the chamber during a specified time period of the test. The analytical technique employed generally determines to a large part the sampling time, and

6. The exposures can be static whereby all of the combustion gases are collected in the exposure chamber during the entire test or dynamic whereby the combustion gases are swept through the exposure chamber and exhausted.

4.2 Medium-scale Tests

Medium-scale tests tend to be smaller than full-scale tests and are typically performed in a large chamber or room. These tests are capable of evaluating composite materials such as a sofa, a television, cable trays full of cable, and similar materials. They can, potentially, simulate a real-world fire, but under conditions that are more controlled than those found in full-scale testing. A major problem in these tests is the control of the temperature of the exposure chamber.

A significant problem with bioassay type medium-scale (and full-scale) test methods is heat build up. The relatively small size of the combustion chamber, as compared to a real-world compartment, confines the heat released from the burning test item, resulting in smoke that is higher in temperature than "normal." When this is transported to the animal exposure chamber, the animals are subjected to temperatures that create their own physiological effects and may aggravate the effects of the toxic materials.. The compensation techniques generally used to counter the problem tend to dilute the products of combustion so that the animals do not get exposed to all of the products generated by the combustion of the sample. The principal rationale for these medium-scale tests is that the actual end-use configuration is tested and the combined effects of the various materials that make up the finished product can be evaluated.

Analytical type medium-scale test methods do not suffer from the heat build up problem, but rely on other data and techniques for the prediction of the synergistic effects of multiple toxicant that may be present. Another problem encountered during medium- and full-scale tests is the location of the analytical measurements. In these types of tests, the combustion by-

products can stratify and the measured concentrations of the various gases will be affected by the measurement location.

4.3 Full-scale Tests

Full-scale tests, as the term implies, typically are conducted in full room or larger compartment, depending upon what is being tested. Like the other test methods described, the predictive ability of full-scale tests is restricted to the exact materials, configuration, and fire scenario tested. These large tests are typically used for an analysis of fire behavior rather than for toxicity testing although several attempts to measure toxicity from full-scale tests have been made [19,20,21]. These tests suffer from the same heat build up limitations as the medium-scale tests. The typical solution entails a remote exposure chamber that is connected to the fire room by ducts which cool the fire gases. The use of ducts risks the adsorption or deposition of important constituent species on the walls of the ducts, changing the exposure. There has not been wide acceptance of these methods to date.

4.4 Bioassay Tests

Biological assay, or bioassay, methods have been used for many years to assess the response of experimental animals to chemical exposures. There is a wide body of evidence to show that the toxicological effects observed in laboratory animals is very similar to those shown in humans [10]. There are some clear physiological differences between man and small rodents that impact combustion toxicology, but the general consensus holds that good quantitative correlation has been observed in the smoke toxicity studies to date.

There is a general consensus that the use of rats or mice is most appropriate for bioassay testing, largely due to the availability of large supplies of these animals and the large body of data available about the animals. Some other studies have been performed using primates and other animals, but these were more for comparison and research purposes than for use as a general toxicity test method [22].

The use of animals for these tests is coming under increasing pressure from animal rights organizations and other sympathetic individuals. This pressure, along with the general uncertainty about the applicability of the results of any standard test method to real-world fire environments, is leading many foreign countries to oppose bioassay test methods. Several European countries are leading a drive in the ISO to adopt analytical test methods as the principal toxicity test method.

4.5 Analytical Tests

With the growing opposition to bioassay methods, analytical techniques are growing in acceptance. These tests can use small-, medium-, or large-scale combustion methods discussed previously and are generally not affected by the heat build up problem that effects bioassay

methods in medium-scale and full-scale tests. In the analytical methods, the sample is combusted in a controlled fashion, and the effluent gases produced are collected and analyzed using standard laboratory techniques. The best of these methods use advanced analytical tools such as FTIR while the simplest methods use colorimetric gas reaction tubes to detect the presence of various effluent gases.

The selection of which gases to monitor and which are most important in the combustion toxicity process remains a disputed matter. In the United States, there is a general consensus that the most important gases are CO, CO_2, O_2, and to a lesser extent, HCN, HCl, and HBr. In the United Kingdom, the established test method (NES 713) measures 15 gases: CO, CO_2, HCN, HCl, HBr, hydrogen sulphide (H_2S), ammonia (NH_3), formaldehyde (HCHO), acrylonitrile (CH_2CHCN), sulphur dioxide (SO_2), nitrogen oxides ($NO + NO_2$), phenol (C_6H_5OH), hydrogen fluoride (HF), and phosgene ($COCl_2$) [23]. Recent proposals in the UK center on measuring the mass loss of the sample during the combustion, and if the mass loss exceeds a predetermined rate, then perform the chemical analysis. France and some other European countries also appear to be interested in this approach.

The principal drawback to the analytical approaches is that you only see what you are looking for. If a specimen produces a unique effluent gas, aerosol or particulate, the analysis may miss it entirely. In fact, the gas analysis does not take into account aerosol particles including, for instance, acids adsorbed on smoke particles which when ingested into the lungs may result in fatal pulmonary edema [24]. The number of potential effluents is very large, and the cost of performing the analysis increases for each species targeted. The concern expressed among advocates of the bioassay methods is that analytical techniques could easily miss such potentially important toxicants as the so-called 'supertoxicants' described earlier, which bioassay tests would identify.

4.6 Current Smoke Toxicity Test Methods

This section reviews the predominant toxicity test methods that are available today and those that have been recently proposed. Out of necessity, only a brief description of each test method is given. Detailed descriptions and procedures can be found in the referenced standards.

4.6.1 NFPA 269

The National Fire Protection Association (NFPA) has adopted NFPA 269, "Standard Test Method For Developing Toxic Potency Data for Use in Fire Hazard Modeling [25]." This is a small-scale test method that uses both analytical and bioassay techniques. In the test, a small specimen is subjected to ignition by exposure to a 50 kW/m^2 radiant flux for 15 minutes. The smoke produced is collected for 30 minutes in a sealed chamber. The concentrations of CO, CO_2 and O_2 are measured over the test period, and a value for the concentration-time product (Ct) is calculated by integration of the area under the concentration-time curves. Measurement of HCN, HCl, and HBr is optional based on the material composition. The Ct product and the mass loss

of the test specimen is used to calculate the FED for the test, and this value is used in a calculation to predict the 30-minute LC_{50} of the specimen. This predicted LC_{50} is then confirmed in a comparable test by exposing six rats to the smoke produced by a specimen sized to produce the predicted LC_{50} of the smoke in the exposure chamber. The number of rats which die during the 30-minute exposure period and the subsequent 14 day post-exposure period determine the validity of the predicted LC_{50}. In this manner, it is possible to ensure that the monitored toxicants actually account for the observed effects. The LC_{50} value that is developed is for a pre-flashover fire and additional calculations are provided such that an LC_{50} (corr) for a post-flashover fire is calculated. This correction factor is based on the increased CO concentration that occurs during post-flashover fires that tend to be ventilation controlled.

A test method similar to the NFPA 269 has been adopted by ASTM. It is ASTM E1678, "Standard Test Method for Measuring Smoke Toxicity for Use in Fire Hazards Analysis" [26]. Currently, the test method is almost identical to the NFPA 269 test method, but it does not contain the post-flashover determination for the LC_{50} (corr). This correction is being processed by ASTM and will probably be included in ASTM E1678 in its next revision.

4.6.2 Royal Navy

In the early 1980's, the British Ministry of Defence issued Naval Engineering Standard (NES) 713, "Determination of the Toxicity Index of the Products of Combustion from Small Specimens of Materials" [23]. This is a small-scale analytical test method. This test uses a Bunsen burner to combust a 100 gram sample in an enclosed chamber. The burner is turned on for as long as it takes to completely combust the specimen, the atmosphere in the chamber is mixed by an internal fan, and then the atmosphere is sampled by drawing samples through a collection of colorimetric gas reaction tubes. There is one tube for each gas monitored: CO, CO_2, HCN, HCl, HBr, HCHO, CH_2CHCN, SO_2, $COCl_2$, H_2S, NH_3, HF, C_6H_5OH, NO, and NO_2. The tubes produce an output in parts per million, which is converted mathematically into a concentration of each gas present in the chamber. From these concentrations, a Toxicity Index is then calculated based on the concentration of each gas monitored. The standard does not directly specify pass/fail criteria but does give guidance about what is acceptable as a Toxicity Index.

4.6.3 International Maritime Organization (IMO)

The IMO has adopted a resolution, Maritime Safety Committee's MSC 41 (64) [27], that adopts ISO 5659, Part 2 [28] and additional test procedures described in the resolution as the toxicity test. This test is a small-scale analytical test method, similar to the NFPA 258 (ASTM E662) smoke box, with modifications to the combustion process. The test uses a cone heater to heat a horizontal sample within the chamber. Samples are exposed to three insults for at least 10 minutes: 25 kW/m^2 piloted ignition, 25 kW/m^2 un-piloted ignition, and 50 kW/m^2 un-piloted ignition. During the test period, the specific optical density of the smoke in the chamber is measured every 5 seconds, and the concentration of CO, CO_2, HCN, HCl, HBr, HCHO,

CH_2CHCN, SO_2, NO, and NO_2, are measured. The draft resolution sets the maximum permissible levels of each gas species for a material to pass the test.

The IMO has also adopted toxicity testing as a part of the High Speed Craft Code [29]. This code, which deals principally with vessels with fiberglass structural elements, adopts the ISO 9705 full-scale corner test [30] and requires FTIR measurements of the smoke for selected species.

4.6.4 International Standards Organization (ISO)

The ISO has adopted ISO 13344, "Determination of the Lethal Toxic Potency of Fire Effluents" [31]. This document is the work of ISO TC92/ SC3 /WG5, "Prediction of Toxic Effects of Fire Effluents." The test method subjects a test specimen to the combustion conditions of a specific laboratory fire model. The standard does not specify the fire model but instead refers to another document ISO TR 9122-4, "Toxicity Testing of Fire Effluents - Part 4" [32]. This document lists and describes several laboratory fire test methods for the generation of combustion gases but does not recommend any specific method. The choice of the combustion model is up to the authority having jurisdiction. The ISO 13344 takes the data obtained from the combustion test and provides guidance on its interpretation. The principles used are similar to the FED and LC_{50} calculations as described in NFPA 269. In the ISO 13344 method, however, no correction for post-flashover fires is provided nor is confirmation testing of the LC_{50} using animals. Animal testing is described in an Annex if it is so desired, and it is similar to that specified in NFPA 269.

Bioassay methods have little support in the European Community. In fact, there is a definite bias against bioassay methods. EC countries (France, UK, Finland, Norway) and Australia prefer some form of analytical approach. The UK proposal for a test for mass loss, followed by chemical analysis if the mass lass rate is "high" is under discussion. France is also showing interest in mass loss. They want to relate mass loss to a toxicity parameter. There is a strong tendency towards FTIR for the analysis method, with a recognition of the need for more than one combustion modality.

4.6.5 DIN 53 436 Method

This is a small-scale test method developed in Germany that uses both analytical and bioassay techniques [33]. This method uses a tube furnace that moves along the test sample at a fixed rate, thermally decomposing a constant quantity of material per unit time. Air flows through the tube throughout the test, and the effluent from the tube is further diluted and cooled with a secondary stream of air before entry into the animal exposure chamber. Several different chambers can be used with the test to permit different animal exposure modes. In most cases, the exposure duration is 30 minutes. In addition to the mortality analysis from the exposed animals, analytical measurements of CO, CO_2, and O_2 are continuously taken through the test, and

periodic measurements of HCN and other selected gases are performed. The standard does not contain pass/fail criteria.

4.6.6 University of Pittsburgh Method (UPITT)

This is a small-scale test method that uses analytical techniques to supplement a bioassay analysis [34]. Small specimens are heated in a Lindberg furnace, and the effluent gases are diluted and cooled as they are transported into the exposure chamber. Four mice are exposed head only, and determinations of sensory irritation, stress index, and lethality are made from observation of the animals. Analytical determinations of the concentrations of CO_2, O_2, and other gases such as HCN, CO, and formaldehyde are made during the test to determine the most likely lethal gases in the effluent. The output of the test is a calculated acute lethal hazard value for the material, which is used for relative comparison between materials.

4.7 Summary of Test Methods

The principal features of the test methods discussed herein are summarized in Table 3. The similarities and differences among the methods follow, to a certain extent, the age of the method development. The current general consensus among fire researchers is that the post-flashover fire poses the greatest threat to human life. Therefore, the more recently developed methods have adopted similar combustion modalities:

- They have adopted exclusively radiant exposure of the samples since radiation is widely accepted as the predominant heat transfer mode and this exposure condition can be used to reproduce a large fire exposure onto the sample; and

- They control the combustion by monitoring the heat flux to the specimen rather than the furnace or flame temperature.

There is not a clear consensus that one rodent is a better human model than another, so there remains the difference among those methods that use bioassay techniques between rats and mice. It is notable that the more recently developed methods have selected rats as the test animal. The newer methods also tend to minimize the use of animals as much as practical and to use them as confirmation of the predicted results obtained via analytical techniques. In this fashion, the genuine concern that a potentially important toxicant such as the so-called ‘supertoxicants’ might slip by undetected is resolved.

The methods do not differ significantly in their chemical analytical techniques, with the notable exception of the NES 713 method which uses colorimetric gas reaction tubes, an outdated and difficult technology. The methods do differ about which gases are most important, but here again we see that the more modern methods seem to be focusing on a standard set of gases.

Table 3. Summary of Smoke Toxicity Test Methods

Method	Combustion Device	Furnace Temperature	Air Flow	Quantity of Material	Number of Animals per Test	Exposure Mode	Exposure Duration	Toxicity Measurements	Chemical Analysis
NFPA 269	Radiant furnace	Fixed, fluxes up to 50 kW/m^2	Static	Surface area varied	6 rats	Head-only	30 min.	LC_{50}/FED 30 min & 14 day	CO, CO_2, O_2, HCN, HCl, HBr
NES 713	Bunsen burner	Burner temperature 1150°C	Static	100 g	N/A	N/A	30 min.	Toxicity index	CO, CO_2, HCN, HCl, HBr, HCHO, CH_2CHCN, SO_2, $COCl_2$, H_2S, NH_3, HF, C_6H_5OH, NO, and NO_2
ISO 5659	Radiant heater	25 or 50 kW/m^2	Static	Fixed size, varied weight	N/A	N/A	10 min.	Specific optical density, gas ppm	CO, CO_2, HCN, HCl, HBr, HCHO, CH_2CHCN, SO_2, NO, and NO_2
ISO 13344	TBD	TBD	Static	TBD	N/A	N/A	30 min.	FED	CO, CO_2, O_2, HCN, HCl
DIN 53 436	Moveable annular tube furnace	Fixed, 200°-600°C	Dynamic	Fixed, same weight or volume	5-20 rats	Head-only or whole body	30 min.	LC_{50} 30 min, & 14 day	CO, CO_2, O_2, selected gases, COHb
UPITT	Tube furnace	Ramped to 600°C above 0.2% weight loss temperature	Dynamic	Varied	4 mice	Head-only	30 min.	LC_{50}, RD50, LT_{50}, 30 min. & 10 min.	CO, CO_2, O_2, HCN, selected gases

Based on the latest actions of NFPA, ASTM and ISO, it appears that use of a combustion model, as described in NFPA 269, the calculation of FED, and the resultant LC50 for both pre-flashover and post-flashover fires, is the most current recommendation for evaluating the toxic potency of smoke.

The current discussion in the international community about the continued use of animal test methods will likely be resolved in the next five years. One proposal is to separate the bioassay method and the analytical method into two separate ISO standards, and to allow the individual nations to select between the two standards. Only time will tell how this is resolved. In the US, the use of bioassay as a final validation of the calculated LC_{50} will likely continue.

5.0 CURRENT REGULATIONS

In the United States, there are no widespread regulations based on smoke toxicity. The current regulations schemes that are in place are discussed below.

5.1 Civilian Regulations

Currently, only two jurisdictions in the US impose smoke toxicity regulations on building and construction materials.

5.1.1 New York State

The State of New York has regulations that specify that all interior finish construction materials must be evaluated for smoke toxicity and reported [35]. The requirements specify the use of the UPitt test method, and the results are filed with the State of New York. The results are placed into a database but there is no regulation concerning pass or fail criterion. The State of New York had hoped that specifiers would utilize the database for materials selection based on smoke toxicity, but in the absence of specific requirements, this has not been done.

5.1.2 City of New York

The City of New York has regulations that specify that all construction materials be evaluated for smoke toxicity [36]. The requirement specifies that materials must demonstrate a toxicity performance (LC_{50}) that is "less than or equal to wood." The UPITT test method is used for this evaluation. The results of the tests are submitted to the MEA of the City of New York, and an approval for use is issued. The test conditions that are specified by the City have been modified such that most materials will meet the intent of the regulation.

5.2 US Navy

5.2.1 General Specifications

In many of the interior finish material or product specifications, the US Navy has a requirement for potentially reporting smoke toxicity results. These reporting requirements are not specifically required as a separate, stand alone requirement but as an extension of a broad toxicity requirement. As an example, MIL SPEC DOD-I-24688, "Insulation Panel, Thermal and Acoustic Absorptive, Open-Cell Polyimide Foam" [37] has the following requirement:

> " 3.17 Toxicity. The material shall have no adverse effect on the health of personnel when used for its intended purpose (see 4.6)." and
>
> "4.6 Toxicity. A manufacturer of material shall disclose the formulation of his product to the Naval Medical Command (MED COM 422), Navy Department, Washington, DC 20372 for approval (see 3.17). The disclosure of proprietary information, which will be held in confidence by the Navy Medical Command, should include the name, formula, and approximate percentage by weight and volume of each ingredient in the product; the results of any toxicological testing of the product; and such other information as may be needed to permit an accurate appraisal of any toxicity problem associated with the handling, storage, application, use, disposal, or **combustion** of the material." (Bold added for emphasis)

Generally, most manufacturers do not submit data with regards to smoke toxicity, and the "combustion" referred to in the standard cited above is interpreted to mean combustion when used for disposal or incineration purposes.

Two US Navy specifications specifically regulate materials based on smoke toxicity. These specifications are MIL-C-24640, "Military Specification for Cable, Electrical, Lightweight for Shipboard Use, General Specification For" [38], and MIL-C-24643A, "Military Specification for Cable and Cords, Electrical Low Smoke, for Shipboard Use, General Specification For" [39]. The regulation is based on tests conducted in accordance with the NES 713 test method. The specific Pass/Fail criteria is based on the NES 713 standard wherein a "Toxicity Index" shall not exceed a value of 1. It is unclear if any other materials have been rejected for use by the US Navy based on toxicity tests.

5.2.2 Submarine Composites

Currently, MIL-STD 2031 (SH), "Fire and Toxicity Test Methods and Qualification Procedure for Composite Material Systems Used In Hull, Machinery, and Structural Applications Inside Naval Submarines," [40] specifies a toxicity test method and provides a pass/fail criteria. The test method is essentially an earlier version of the NFPA 269 test method. In the MIL-STD, the combustion device is a furnace (known as the Potts furnace) that was used in the initial

research on smoke toxicity. This furnace has been replaced with a radiant heater furnace. The MIL-STD requires the following:

1. An LC_{50} be developed using combustion gas analysis for CO, CO_2, O_2 and HCN. The LC_{50} value is calculated based on the N-GAS Model;

2. A bioassay test is performed at 80 percent of the LC_{50}; and

3. If no animals die, then the material passes the test.

In essence, this test was designed to screen materials or products for unusual gases that may be generated by the burning of the materials or products. If the material or product fails the test, then other combustion products beyond CO, CO_2, low O_2, or HCN must be responsible for the animal deaths.

This test was placed into the MIL-STD due to the nature of the new and future materials being used in composite technology. With the advent of these novel materials, there was, and still is, very little experience with respect to their combustion toxicity, in either the civilian or military environments. Therefore, it was felt that some toxicity screening was prudent prior to their extensive use onboard ships and especially in enclosed submarine applications.

5.3 Use of Regulations

As discussed, very little regulation is currently imposed on materials based on smoke toxicity. Most of the regulations consist of submitting data and very little use of a specific criteria is imposed. Also, the tests that are generally used are tests that no longer have wide acceptance in the smoke toxicology community.

With the codification of the NFPA, ASTM, and ISO test methods for measuring the toxic potency of smoke, it is expected that regulations will be imposed using these test methods. In the U.S., the first use will probably be by the NFPA National Electrical Code [41], such that a criteria for the toxicity of electrical cable can be set similar to the requirements for low flame spread and low smoke electrical cable. The use of the tests with respect to setting specific limits is unclear at this time. For pre-flashover fires, the LC_{50} of materials and products will be probably be developed using a combination of analytical modeling and the demonstrated performance of existing materials. The post-flashover fire scenario will be easier since in this condition, the CO generation of the fire is anticipated to be the greatest factor. As described in the Appendix of NFPA 269, the LC_{50} (corr) values for materials that are greater than 8 g/m^3 are indistinguishable from each other. This is based on the production of CO from post-flashover fires and the sensitivity of the current test method. Most common building materials have LC_{50} (corr) values greater than 8 g/m^3.

6.0 CONTROL OF SMOKE AND TOXIC GASES ONBOARD US NAVY SHIPS

Fires onboard US Naval ships are a serious concern since the mission of the ship cannot be compromised in the event of a fire and there is limited capability to escape. Due to the nature of operations, crew members are constantly available for detection and suppression operations. As such, many fires can be controlled early, and if a fire does continue to grow, additional firefighting capabilities can be brought to bear. In this environment, detection of a fire can occur fairly rapidly and fire fighting operations are initiated upon detection.

Smoke and fire gases are controlled and contained on US Navy ships by both active and passive intervention. If suppression systems are installed, smoke generation is limited by controlling fire growth and spread. Depending on the type and location of the suppression system, actuation may be by automatic or manual means. If there is no installed suppression system, and fire growth is not interrupted in the incipient stages, a fire party is dispatched to deal with the incident in accordance with NSTM 555 [42]. Firefighters would respond with full protective ensembles which include breathing apparatus. Depending on the size of the incident, initial smoke control actions would involve shutting closures (i.e., doors, hatches, scuttles and ventilation dampers) to the affected space and securing ventilation. If there is significant smoke spread or the potential for smoke spread, smoke boundaries might be established using installed closures or portable smoke curtains. The smoke boundaries might be established within a fire zone or concurrent with fire boundaries. Outside these boundaries, spaces should be tenable for unprotected personnel.

For larger or difficult fires, active ventilation might be used in conjunction with active firefighting to improve visibility and reduce heat. Ventilation paths to weather might be established using passageways, smoke curtains, and portable desmoking equipment. Use of installed ventilation for active smoke control is not currently recommended since existing systems cannot be readily configured, aligned, nor operated for smoke control. The new ship class LPD 17 will have a smoke ejection system (SES) with the capability to exhaust the Damage Control (DC) deck. Testing is underway to establish appropriate doctrine and tactics for ships with SES along with expanding the potential smoke control usefulness of the SES.

There also exists, on surface combatants, a greater than 100 percent compliment of emergency breathing devices (EBD), each supplying approximately 15 minutes of oxygen. A new device was recently issues to watch standers and others entering machinery spaces on combatants, known as emergency escape breathing devices (EEBD), each containing ~2-5 minutes of breathing air.

7.0 DISCUSSION

The fire death data reported to date show that the majority of fire deaths are due to smoke inhalation. Generally, fire deaths due to smoke inhalation occur when the victim is remote from

the fire and the fire has proceeded to flashover. Also, the data support the supposition that the majority of fire deaths are due to carbon monoxide. This development of toxic hazard can be illustrated using data from full-scale fire tests. A fire test of a fully outfitted DDG-51 Chief Petty Officer in the Berthing space was conducted aboard the ex-USS SHADWELL [43]. Figure 1 provides a plot of the conditions attained in the test room. The data show that obscuration is attained prior to significantly hazardous conditions and as the fire approached flashover conditions, life threatening conditions for CO, O_2 depletions, and temperatures were attained.

As a further demonstration of toxic hazard, four full-scale fire tests were conducted in a fully furnished simulated hotel room with an attached corridor and remote room [21,44]. Figure 2 provides a sketch of the experimental arrangement. During the tests, the door from the fire room to the corridor was fully open. The door between the corridor and the remote room was open approximately 1 in. (2.5 cm) until approximately 3 minutes after flashover, when it was closed to prevent the development of excessive concentrations of heat and combustion products.

The sequence of events that occurred in the burn room are shown in Figure 3. The tests were initiated with a smoldering fire in the chair closest to the sofa. During the smoldering phase of approximately 19 minutes, no conditions were attained which would be considered hazardous to life. Following flaming ignition of the chair, the fire progressed rapidly to flashover within approximately 8 minutes, accompanied by life-threatening conditions of temperature, CO, HCN, and O_2 depletion in the room of origin. After flashover in the burn room, tenability in the remote room also quickly deteriorated as shown in Figure 4, first with visual obscuration by smoke, followed by rapidly increasing concentrations of toxic gases. Test animals (rats) in the remote room became incapacitated within approximately 2 minutes, with death occurring from carbon monoxide asphyxiation approximately 11 minutes after flashover. From present knowledge of carbon monoxide intoxication, it is likely that humans in the remote room would have been incapacitated and killed in approximately the same intervals.

It was considered significant in these tests that the toxic hazard did not develop until flashover was approached in the burn room. After flashover, tenability conditions were rapidly exceeded in the burn room, the corridor, and the remote room.

These data exemplify the toxic hazard approach to smoke toxicity. In this approach, if a fire can be contained and is not allowed to progress to flashover, toxic hazards are reduced as follows:

- less combustion gases being produced especially CO,
- less visible smoke is released,
- lower temperatures occur, and
- less potential for fire spread to other materials or areas.

The full-scale test data also demonstrate that toxic hazard is comprised of several components such as heat, visible smoke, toxic gases, and flames. For personnel involved in initial fire

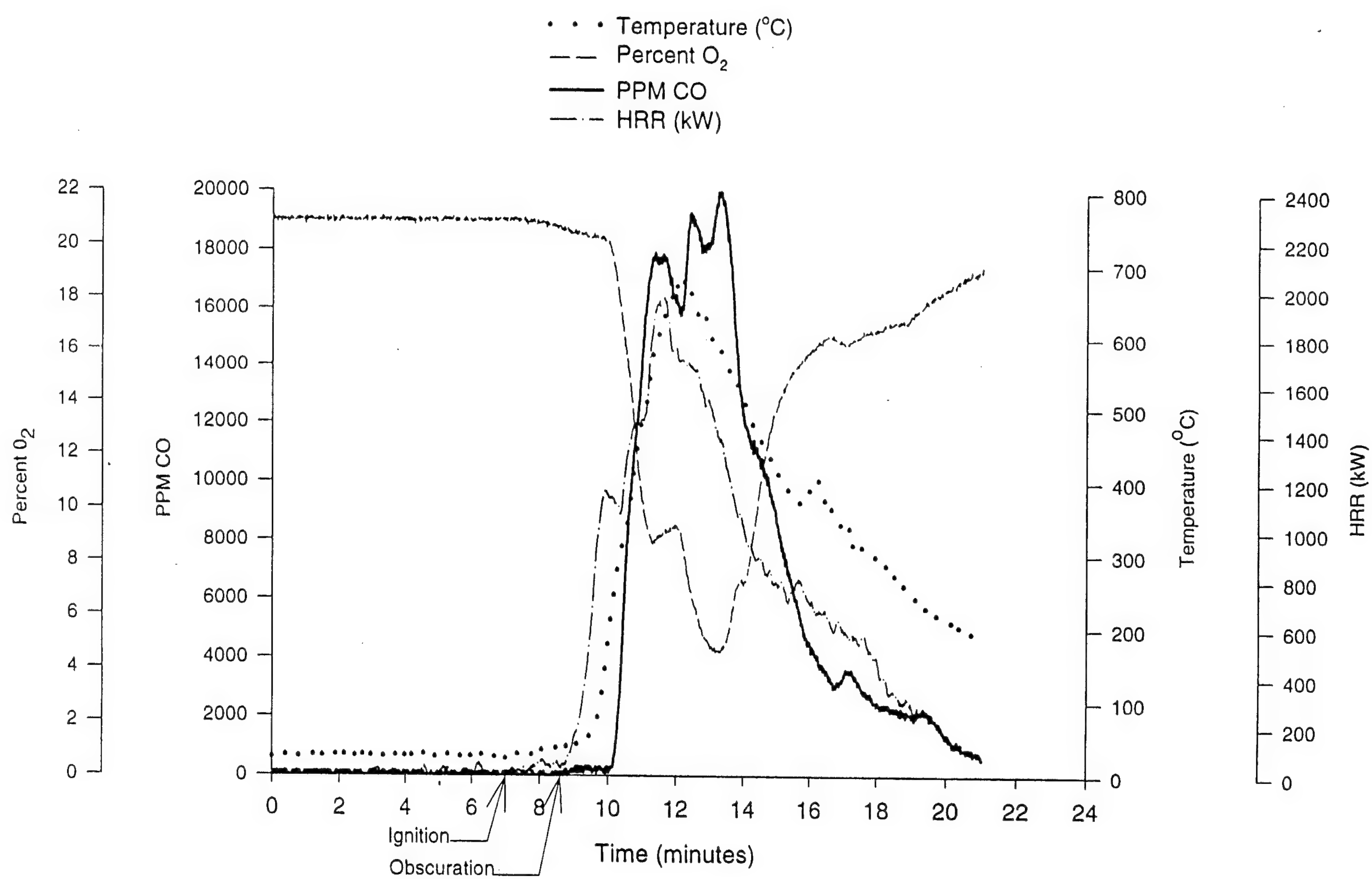

Fig. 1 – Test room conditions

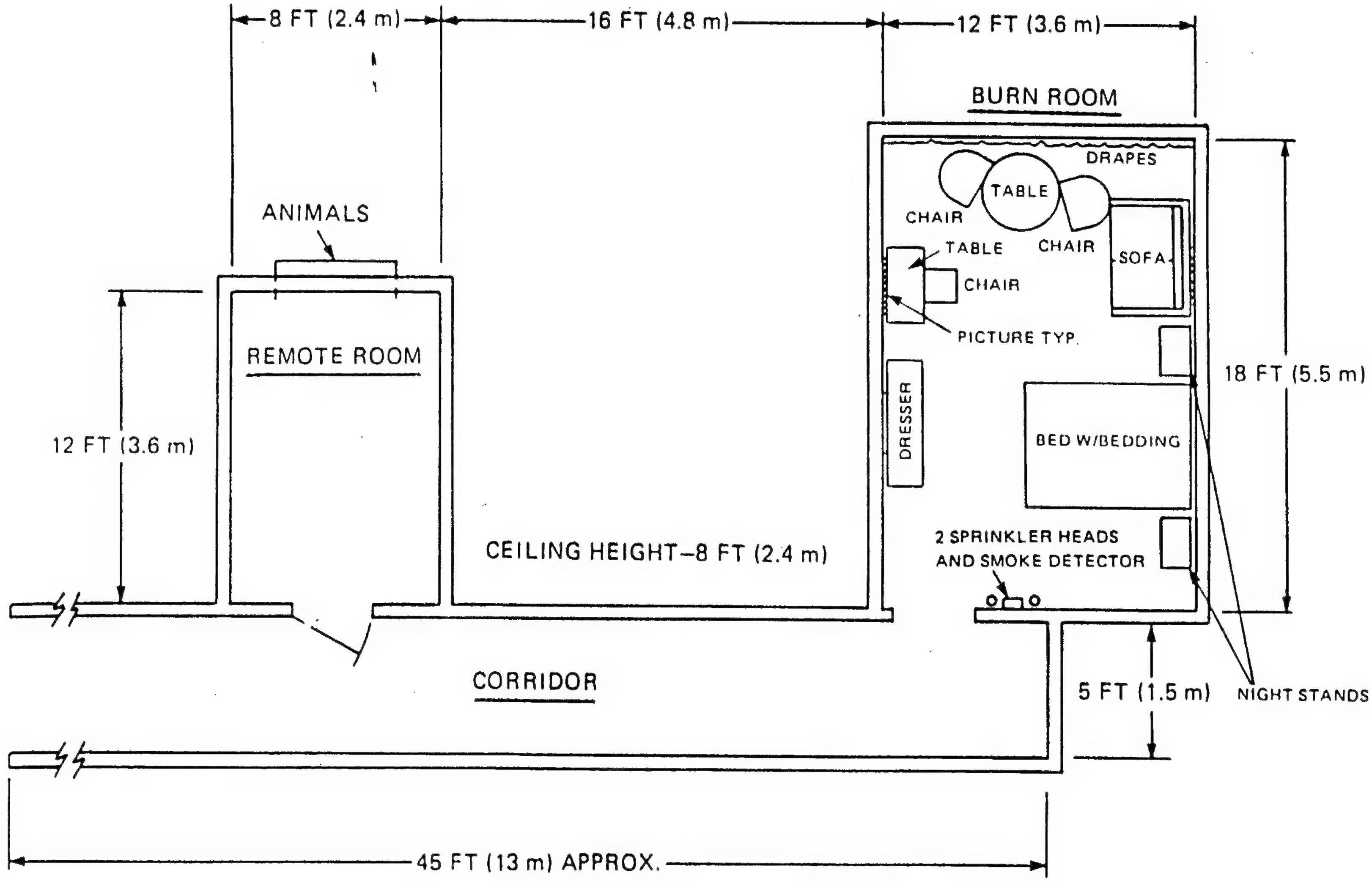

Fig. 2 - Burn room, corridor, and remote room full-scale test facility at Southwest Research Institute

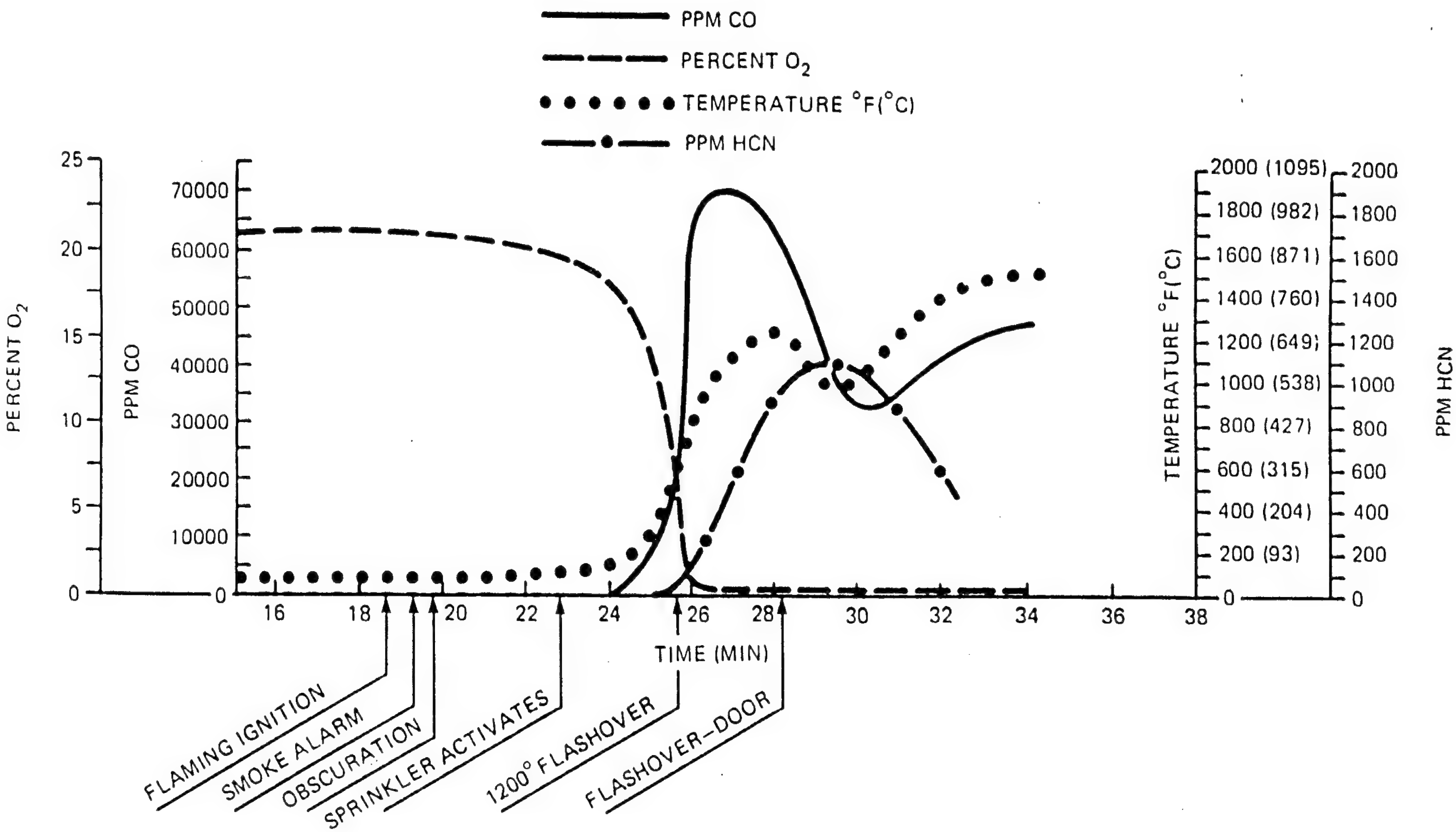

Fig. 3 – Composite illustration of events and development of hazardous conditions at the 1.7 m (5.5 ft) level in the burn room during fully furnished room fires conducted at Southwest Research Institute

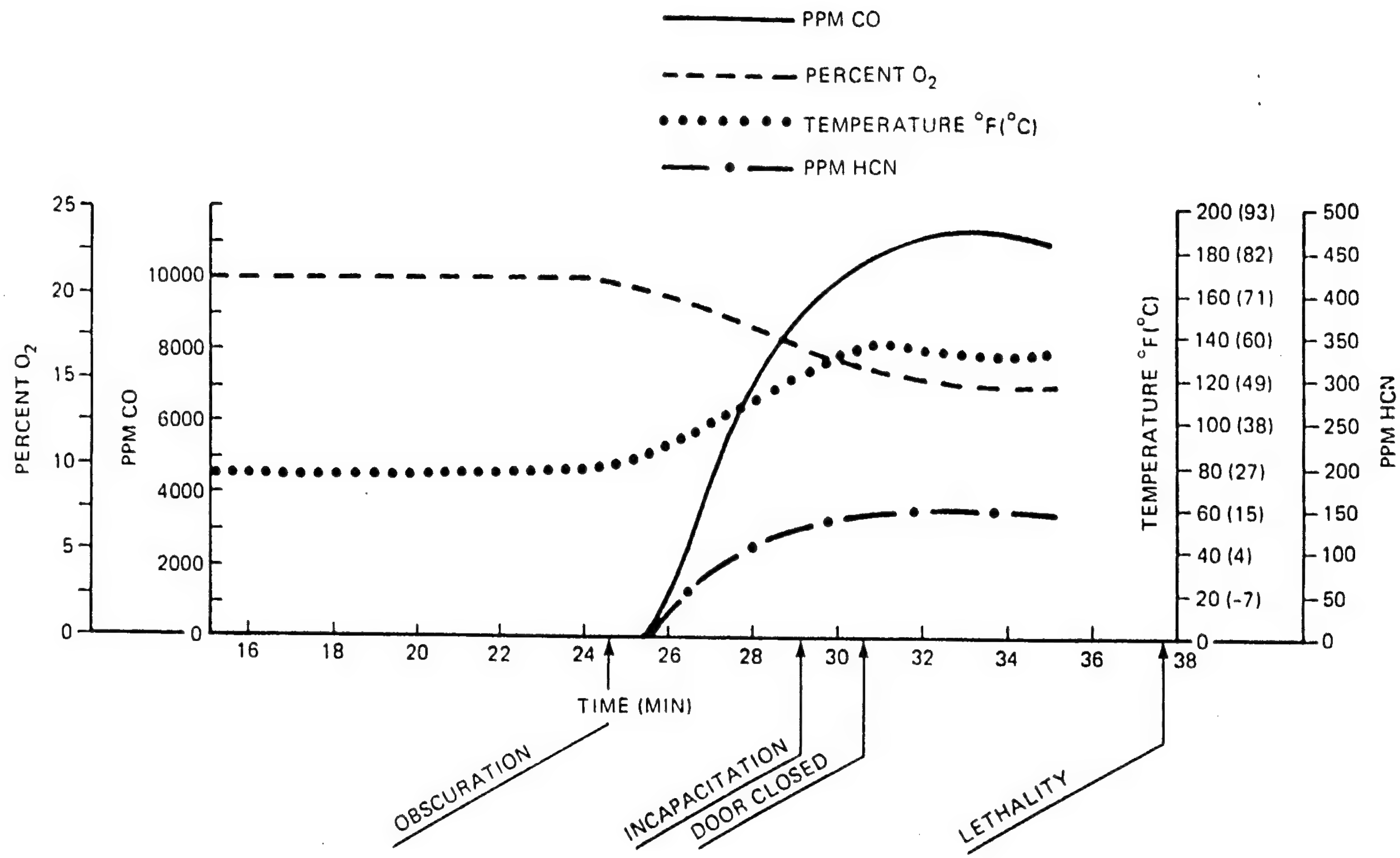

Fig. 4 - Composite illustration of events and development of hazardous conditions at the 1.7 m (5.5 ft) level in the remote room during fully furnished room fires conducted at Southwest Research Institute

fighting duties and who are intimate with the fire, toxic gases are generally a secondary concern compared to the visible smoke, heat, and flames. This has been demonstrated in previous work involving anti-sweat pipe insulation [44]. Within the fire compartment, analytical modeling based on experimental data showed that the initial insults will be visible smoke and heat. In the context of the US Navy, the toxicity of the combustion gases are the greatest threat to the large number of personnel who are remote from the fire.

Since fires do not occur in a controlled manner and many different types of materials and products can be involved, the materials approach to toxicity (i.e., a materials toxic potency is of primary importance) cannot be ignored. As shown with the newer composite materials, a screening test to evaluate a materials toxic potency may have merit. The US Navy uses some materials that are not in extensive use in building construction throughout the civilian world, and as such, these materials may pose a threat since very little fire performance, smoke, and toxicity experience has been gained by their naval use. Examples of these are polychloroprene mattresses, polyimide insulations, etc. This approach would suggest that a small-scale toxicity test be used to at least screen material toxicity.

All of the smoke toxicity tests that have been reviewed suffer from the overall problem that only a single fire scenario is simulated. As discussed earlier, the toxic hazard of a fire is influenced by many variables such that material toxicity may change based on the fire scenario [10] . For example, PTFE when tested in one toxicity test method decomposes to form a highly toxic lung irritant which causes death at concentrations of two to three orders of magnitude less than that of other polymeric materials. In another toxicity test, the magnitude is approximately 20 percent less toxic, and in a third toxicity test, a further three times less toxic although still somewhat more toxic than most other materials. However, when decomposed in a manner different than from any of the previous tests, the high toxic potency is eliminated, and it is possible that, under real fire conditions, the products of combustion may not exhibit any unusual toxic potency. This illustrates the potential problem with standardized small-scale toxicity tests. The toxic potency or the toxic hazard of a material or product is not necessarily an intrinsic property of the material or product but is a function of the fire scenario.

For the US Navy, the current approach to the combustion toxicity of materials can be summarized as "Keep Fires Small." This philosophy was initially developed with respect to the flammability of materials such that fires cannot produce significant quantities of heat, flames, or smoke. This approach controls the toxic hazard of a fire. This can only be accomplished, however, by the complete use of materials that exhibit low flammability, low ignition potential, and low heat release. Onboard Navy ships, this is currently an impossible task, and fires will continue to occur. Additional resources such as training, fire detection, and suppression (manual and automatic) are required so that if a fire does grow, there is an appropriate level of intervention. As a last resort, assuming a fire is not immediately controlled (i.e., weapons impact), the ship design must provide a means for compartmentation and smoke removal so that firefighting efforts can continue along with protection of remote personnel.

The use of a toxicity potency test for materials would add another criterion to the list of desired properties of materials used by the US Navy. While a small-scale toxic potency test has limitations, so do many of the other fire tests currently used to evaluate materials. For example, many of the fire tests are scenario dependant based on the fire exposure used in the test. Also, the use of a toxic potency test for materials is not without precedence in the US Navy as shown by MIL-STD 2031 for composites onboard submarines and MIL-C-24640 and MIL-C-24643A for electrical cables.

While the use of a toxic potency test may initially appear to be appropriate, it is important to assess which materials to apply the requirements. The newer materials, such as composites, are possible candidates for regulation but should the regulation be extended to other materials currently in use? Examples are furnishings, insulations, interior finish items, etc. The argument can be made that testing of all potentially combustible materials should be performed. In reality, many of the existing materials would probably show that they do not have a significant toxic potency when compared to other materials, but this has not been demonstrated via actual tests.

If a toxic potency test is desired, then it is recommended that the NFPA 269 test method be used. This test provides an appropriate screening method for materials based on current knowledge in the fire toxicity community. The test must be conducted at a specified heat flux exposure, such as 50 kW/m^2, for all materials. Even if a material does not ignite or burn at this exposure, then it is a valid test based on the insult that is given to the sample. In order to easily compare materials, a single heat flux must be chosen and used. An incident heat flux of 50 kW/m^2 appears to be reasonable for common building materials and, as a such, was chosen for use in NFPA 269. If the Navy decides a higher heat exposure is appropriate, then a higher heat flux such as 75 kW/m^2 can be selected.

It is also suggested that, if this method is adopted, two "pass/fail" criteria be used:

- the calculated LC_{50} value be confirmed via animal tests, and
- the LC_{50} (corr) value (post-flashover fire) be greater than 8 g/m^3.

The greatest threat to remote personnel still remains the post-flashover fire, and if a material exhibits an unusual toxicity in this realm of a fire, then that behavior should be identified. This criterion will, of course, still allow a potential problem to exist for those personnel that are intimate with a small or growing fire prior to flashover or during the donning of EBAs in an unprotected area.

The NFPA 269 test method is an industry consensus method and potentially can be performed by several commercial testing laboratories. Due to the current low demand for these tests, the commercial laboratories have "moth-balled" the equipment, but it is available for future tests.

8.0 SUMMARY AND RECOMMENDATIONS

In the event of a fire, all combustible materials and products will exhibit a toxic hazard. The size and impact of the hazard is dependant on many variables and the response of the material to the specific fire scenario. Toxic potency is but one of the many parts of toxic hazard. While it is advisable to control all aspects of toxic hazard, many materials cannot be regulated in this manner. Materials such as diesel fuel have a toxic hazard via their ignition temperature, flammability, and smoke generation. These fire performance properties may be more significant than the toxic potency of the diesel fuel. This analysis has only considered the toxic potency portion of the toxic hazard. As such, several options are available to the US Navy to address this issue:

Option 1 – This option consists of limiting regulatory actions to the current procedures or practices. This option recognizes that control of the flammability of material or products is the most important criterion and that, while some materials may have different toxic potencies, the majority of materials will probably have similar toxic potencies. This option also assumes that continued work with respect to a reduction of materials' flammability will continue so as to provide further assurance that fires will not grow significantly. This option also assumes that, as required by MIL-STD 2031, composites used onboard submarines will continue to be tested. It is recommended, however, that this specification, along with MIL-C-24640 and MIL-C-24643A, be updated to require the use of NFPA 269 and the "pass/fail" criterion previously recommended. The primary advantage of this option is that no new regulations, etc. are imposed. The disadvantage of this option is that toxic potency is ignored except for several limited applications. This option, from a toxic potency view, has the greatest risk.

Option 2 – This option is similar to Option 1 except that all newer materials such as composites be tested for toxic potency without regard for the location of their use on either submarines or surface ships. This option will have the advantage of providing toxic potency screening for new and novel materials and over time, as the use of these materials increases, then data are available. It will also provide a measure of assurance that these materials can be used in other areas or applications without concerns over their toxic potency. The disadvantage of this option is establishing who will determine which materials will be tested and under what methodology. Should this increased regulation be applied to only materials identified as "composites" or should other new or novel types of materials be included? It is recommended that if this option is selected, then other new or novel materials should be included. A selection based on chemical formulation and usage might be an initial approach. This option carries less risk, from a toxic potency view, than Option 1.

Option 3 – This option would require that all combustible materials used onboard US Navy ships be evaluated for their toxic potency. This evaluation would be an additional criterion that would be added to the currently established criterion for the material or product. The

advantage of this approach is that toxic potency data would be available for all combustible materials, and as such, appropriate decisions could be made concerning their use. The disadvantage of this approach would be that all specifications, etc. would have to be revised to incorporate this evaluation and the manufacturers would have to provide the data. This option, from a toxic potency view, carries the least risk.

As stated earlier, all combustible materials, when involved in a fire, will exhibit a toxic hazard. The toxic potency of a material is but one element of the overall toxic hazard. If a toxic potency test as described earlier is adopted, it will provide some assurance that a "supertoxicant" or at least a very toxic material would not be generated under a specific fire condition. It should be noted that very few "supertoxicants" have ever been identified, but as new polymers, etc. are developed, this may occur again. Since the US Navy is actively pursuing these use of new and novel types of materials, and since the US Navy has a high potential for shipboard personnel to be exposed to smoke from a fire, it is necessary for the US Navy to make a decision with regards to toxic potency of materials.

Three options have been presented, and each option carries advantages and disadvantages along with different risk potential. At this time, our recommendation is that the US Navy adopt the option with the least risk and the greatest potential protection for personnel - Option 3. The final decision as to which option is selected will, however, reside with the US Navy based on their best judgement and risk analysis.

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